

UTILITY PATENT APPLICATION TRANSMITTAL <small>(Only for new nonprovisional applications under 37 CFR 1.53(b))</small>		Attorney Docket No. IJ-0005 First Named Inventor or Application Identifier Loretta Ann Grezzo Page Express Mail Label No. EE655208562US Express Mailing Date July 22, 1998
APPLICATION ELEMENTS <small>See MPEP chapter 600 concerning utility patent application contents.</small>		ADDRESS TO: Assistant Commissioner for Patents Box Patent Application Washington, DC 20231
<p>1. <input checked="" type="checkbox"/> Fee (Authority to charge deposit account below.) <small>(Submit an original, and a duplicate for fee processing)</small></p> <p>2. <input checked="" type="checkbox"/> Specification [Total Pages 12] 1</p> <ul style="list-style-type: none"> - Descriptive title of the invention - Cross References to Related Applications <i>(if needed)</i> - Statement Regarding Fed sponsored R & D <i>(if needed)</i> - Reference to Microfiche Appendix <i>(if filed)</i> - Background of the Invention - Brief Summary of the Invention - Brief Description of the Drawings <i>(if filed)</i> - Detailed Description - Claim(s) - Abstract of the Disclosure <p><input type="checkbox"/> Drawing(s) (35 USC 113) [Total Sheets 0]</p> <p><input checked="" type="checkbox"/> Oath or Declaration [Total Pages 1]</p> <p>a. <input checked="" type="checkbox"/> Newly executed (original or copy)</p> <p>b. <input type="checkbox"/> Copy from a prior application (37 CFR 1.63(d)) <small>(for continuation/divisional with Box 14 completed)</small></p> <p>i. <input type="checkbox"/> DELETION OF INVENTORS Signed Statement below at 15 deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).</p> <p>5. <input type="checkbox"/> Incorporation by Reference <i>(useable if Box 4b is checked)</i> The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.</p>		<p>6. <input type="checkbox"/> Microfiche Computer Program (Appendix)</p> <p>7. <input type="checkbox"/> Nucleotide and/or Amino Acid Sequence Submission <small>(if applicable, all necessary)</small> <ul style="list-style-type: none"> a. <input type="checkbox"/> Computer Readable Copy b. <input type="checkbox"/> Paper Copy (identical to computer copy) c. <input type="checkbox"/> Statement verifying identity of above copies </p>
ACCOMPANYING APPLICATION PARTS		
<p>8. <input checked="" type="checkbox"/> Power of Attorney</p> <p>9. <input type="checkbox"/> Information Disclosure Statement (IDS)/Cover Letter plus PTO-1449</p>		<input type="checkbox"/> Copies of IDS Citations
<p>10. <input type="checkbox"/> Preliminary Amendment</p> <p>11. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) <small>(Should be specifically itemized)</small></p> <p>12. <input type="checkbox"/> Certified Copy of Priority Document(s) <small>(if foreign priority is claimed)</small></p> <p>13. <input type="checkbox"/> Other:</p>		
14. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:		
<input type="checkbox"/> Continuation <input type="checkbox"/> Divisional <input type="checkbox"/> Continuation-in-part (CIP) of prior Application No.: _____		
15. <input type="checkbox"/> DELETION OF INVENTOR(S) STATEMENT: This application is being filed by less than all the inventors named in the prior application. In accordance with 37 CFR 1.63(d)(2) and 1.33(b), the Assistant Commissioner is requested to delete the name(s) of the following person or persons who are not inventors of the invention being claimed in this application:		
16. <input type="checkbox"/> Amend the specification by inserting before the first line the sentence: -- This is a <input type="checkbox"/> continuation-in-part, <input type="checkbox"/> continuation, <input type="checkbox"/> division of Application No. _____ filed , now abandoned. --		
17. <input type="checkbox"/> Cancel in this application original claims _____ of the prior application before calculating the filing. (At least one original independent claim must be retained for filing purposes.)		
18. <input type="checkbox"/> Priority of foreign Application No. _____ filed on _____ in _____ _____ is claimed under 35 U.S.C. 119. _____ (country)		

CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS (37 CFR 1.16(c))	12 - 20 =	0	x \$ 22 =	0
	INDEPENDENT CLAIMS (37 CFR 1.16(b))	3 - 3 =	0	x \$ 82 =	0
	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 270 =	0
				BASIC FEE (37 CFR 1.16(a))	+ \$ 790.00
				TOTAL =	\$ 790.00

19. The Commissioner is hereby authorized to credit overpayments or charge the following fees to Deposit Account No. 04-1928:

a. Fees required under 37 CFR 1.16.

b. Fees required under 37 CFR 1.17.

20. Other:

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22. SIGNATURE OF ATTORNEY OR AGENT REQUIRED

NAME	Joseph A. Tessari	REG. NO.: 32,177
SIGNATURE		
DATE	July 22, 1998	

WATER INSOLUBLE NON-IONIC GRAFT COPOLYMERS

Background of the Invention

This invention relates to polymers and, more particularly, to non-ionic graft copolymers that are soluble in aqueous vehicles but are substantially insoluble in water. The graft copolymers are particularly useful as film-forming binders in aqueous dispersions, such as paints or inks, and overcoat compositions.

For many reasons, aqueous dispersions are widely used as coating compositions, such as paints and inks. While these aqueous dispersions have the obvious environmental benefits over their solvent-based counterparts, the aqueous nature of the dispersion creates some unique disadvantages. For instance, the components in an aqueous dispersion need to be soluble or dispersible in the vehicle, which is mostly water. Thus, the coating tends to be sensitive to water or high moisture, which makes it unsuitable for many of its intended applications.

To overcome this problem, a class of polymers known as binders has been developed. These binders, when added to the coating composition, are intended to function as film forming agents that effectively bind the various components of the coating together, particularly the pigment particles used in such coatings, as the coating dries or cures. The use of a proper binder can dramatically improve certain properties of the coating, such as resistance to smear, abrasion, water and washing (i.e., detergents).

An additional challenge is presented in selecting binders for ink applications, particularly ink jet inks. Ink jet ink printing is a form of digital printing in which droplets of ink are made to be ejected (i.e., "fire") from an orifice in a printhead or a spray nozzle in response to an electronic signal from, for example, a computer. Examples of ink jet printing include the thermal ink jet printing, piezoelectric ink jet printing, continuous ink jet printing and air brush printing.

While paints and other coating applications can be in a variety of ways, ink jet inks must be applied by ejecting or jetting small droplets of ink from an orifice in a printhead. In addition, the ink must be formulated such that it will not form a film on the components of the printhead (e.g., resistors used in thermal ink jet printheads), won't puddle on the orifice plate, and won't dry out and clog the openings in the orifice plate. Further, ink jet inks have a much narrower viscosity tolerance than do paints or similar coating applications. Thus, it is far more difficult to formulate ink jet inks as compared to other coatings and, in particular,

the requirements of the binder polymer are significantly more demanding. For example, whereas a paint might be formulated to contain 30-40% by weight of a binder polymer, an ink cannot tolerate more than about 20% as a theoretical maximum given the current printhead technology and, in most prior art, the binder content cannot exceed about 2-4% by weight of the ink composition.

5 In the past decade, ink jet printing, particularly the thermal and piezo forms, has become extremely popular for home office, small office and personal printer applications, primarily due to its relatively low cost, speed and quiet operation. In 10 more recent years, the popularity of ink jet printing has increased even further due to the introduction of systems (printers, software, media and inks) offering very high quality (near photographic) color and graphics capabilities. As the capabilities of ink jet technology increase, the use of such technology has expanded into other market segments, such as in large format and very large 15 format applications. In general, the terms "large format" and "very large format" are used to define a class of printers that operate with a particular size media. For example, large format is commonly used to mean printers utilize media of not less than 17 inches in the smallest dimension and very large format is normally used to mean printers that utilize media of not less than about 60 inches in the smallest 20 dimension. Such printers are used for applications such as banners, signage, displays, posters, billboards, as well as textile printing applications for clothing, fabrics, draperies and similar applications.

25 The use of ink jet printing in the large and very large format applications (for convenience, collectively referred to as "large format") has important advantages, not the least of which is the savings in short production runs over more traditional analogue printing methods. Yet, there are also disadvantages. For example, the types of final products produced for these applications may be subject to the 30 elements in outdoor usage (e.g. billboard or awning applications), laundering (e.g., clothing applications), abrasive friction (e.g., automobile interior fabrics), etc. and thus need to be far more lightfast, waterfast, washfast and abrasion resistant than typically required for office or home printing applications. While much improvement has been made in enhancing lightfastness and waterfastness of ink jet inks in recent past, due to the use of pigment colorants, there is a need in the art 35 for improving the resistance of ink jet inks to smear, abrasion and washing.

Summary of the Invention

In one aspect, the invention comprises a non-ionic graft copolymer binder having a hydrophobic backbone and non-ionic, hydrophilic side chains, which binder is soluble in an aqueous vehicle but substantially insoluble in water.

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In another aspect, the invention comprises an aqueous coating composition comprising

a) an aqueous vehicle comprising no more than 80% by weight water, the remainder of the vehicle comprising water soluble or water miscible organic co-solvents;

b) a non-ionic graft copolymer binder having a hydrophobic backbone and non-ionic, hydrophilic side chains, which binder is soluble in the aqueous vehicle but substantially insoluble in water.

10 15 In yet another aspect, the invention comprises a washfast, detergent-resistant aqueous ink particularly suited for textile printing, comprising:

a) an aqueous vehicle comprising no more than 80% by weight water, the remainder of the vehicle comprising water soluble or water miscible organic co-solvents;

b) an insoluble colorant, preferably a pigment and polymeric dispersant; and

c) a non-ionic graft copolymer binder having a hydrophobic backbone and non-ionic, hydrophilic side chains, which binder is soluble in the aqueous vehicle but substantially insoluble in water.

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Detail Description of the Embodiments

The invention provides a non-ionic graft copolymer binder and an aqueous coating composition containing same, that is particularly suitable for use in aqueous pigmented ink jet inks. Inks incorporating these graft copolymers are disclosed in co-pending US Application No. ____ / _____, filed contemporaneously herewith (Docket No. IJ-0007), the disclosure of which is incorporated herein by reference.

Aqueous Vehicle

The aqueous vehicle is a mixture of water and at least one co-solvent and comprises no more than 80% by weight, of water. The co-solvent used is determined primarily by the end use application. However, the co-solvent is typically water soluble or water miscible so as to form a single phase vehicle with water.

The precise composition of the aqueous vehicle will vary depending upon the type of composition being made, its ultimate use, the method of applying the composition, the type of substrate being coated and the other ingredients in the composition. Generally speaking for ink applications, the vehicle comprises preferably 60-70% water, with the balance being a mixture of one or more glycols, a glycol ethers and pyrrolidones. Representative water-miscible or water soluble co-solvents for ink applications are disclosed in US 5,221,334, incorporated herein by reference.

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Non-ionic Graft Copolymer

The graft copolymers of this invention comprise a hydrophobic backbone with non-ionic, hydrophilic side chains. The copolymers are soluble in the vehicle, but substantially insoluble in water.

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The non-ionic hydrophilic side chains of the graft copolymer comprise macromonomers which are soluble in water but are insoluble in non-polar organic solvents. The water-solubility of these macromonomers enable the graft copolymer to be miscible in an aqueous vehicle. The non-ionic nature of the side chain allows the binder to be washfast even to soaps and detergents, which are generally anionic or cationic and will solubilize species of the opposite ionic charge. The non-ionic nature of the side chains also reduces the risk of corrosion of metal pens or other application devices. The macromonomers are made from non-ionic monomers such as ethoxytriethylene glycol methacrylate, methoxypolyethylene oxide methacrylate, methoxypolyethylene oxide acrylate, polyethylenoxide methacrylate, polyethylene oxide acrylate, N-vinyl pyrrolidone and the like.

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The hydrophobic backbone serves as the water-insoluble, abrasion resistant portion of the binder. By selecting monomers of appropriate glass transition temperatures and crystallinities, binder properties such as hardness, flexibility, and durability can be adjusted. The hydrophobic backbone of the graft copolymer is prepared from monomers such as methyl acrylate, methyl methacrylate, styrene, alpha-methyl styrene, phenyl acrylate, phenyl methacrylate, benzyl acrylate, benzyl methacrylate, 2-phenylethyl acrylate, 2-phenylethyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, 2-naphthyl methacrylate, p-nitrophenyl acrylate, p-nitrophenyl methacrylate, phthalimidomethyl acrylate, phthalimidomethyl

methacrylate, N-phenyl acrylamide, N-phenyl methacrylamide, N-benzyl acrylamide, N-(2-phenylethyl)acrylamide, N-(2-phthalimidoethoxymethyl)acrylamide, vinyl benzoate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, ethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, vinyl acetate, vinyl butyrate, and the like.

5 The hydrophobic backbone may contain up to 30% by weight, based on the total weight of the graft copolymer, of a hydrophilic non-ionic monomer, as listed above. Similarly, the hydrophilic side chains may contain up to 30% by weight, 10 based on total weight of the graft copolymer, of a hydrophobic monomer, as listed above. The side chains have a number average molecular weight of at least 500, preferably 1,000 - 2,000. The side chains comprise 15 - 60% by weight of the graft copolymer, preferably 20 -50%. By adjusting the hydrophilic/hydrophobic balance of the backbone and side chains, the binder can be tailored for solubility 15 in aqueous vehicles, while in itself being water insoluble.

Although random copolymers can be used as binders, they are not as effective in solubility and durability properties as graft copolymers. Since random copolymers exhibit the average properties of the individual monomers, balancing 20 properties to yield binders which are soluble in aqueous vehicle while being substantially insoluble in water, which are durable, abrasion resistant and flexible, and which can be reliably applied from demanding devices such as an ink jet head is very difficult, if not impossible, to achieve.

25 The graft copolymers are prepared using standard grafting techniques known to those skilled in the polymer art. Particular synthesis techniques and conditions are set forth in the examples.

Other Ingredients

30 The coating compositions encompassed by this invention can contain other ingredients as desired for the particular application. For example, if the composition is intended for use as an ink, a pigment and dispersant, or a dye colorant can be added, as is known in the art. In addition, standard ink adjuvants such as surfactants, biocides, sequestering agents, humectants, coalescents, 35 viscosity modifiers, defoaming agents, UV absorbers, corrosion inhibitors, and the like may be used to advantage. Many of these types of additives are also used in other coating compositions (e.g., paints), although the precise compound used in each application is likely to be different.

For example, when the coating composition is intended for use as an overcoat composition to protect images on vinyl and other hydrophobic substrates, it has been found advantageous to incorporate a silicone or fluorinated surfactant. Such 5 surfactants are disclosed in co-pending US Patent Application No. 08/867,373, filed June 2, 1997, the disclosure of which is incorporated herein by reference. Particularly preferred are the BYK brand of silicone surfactants from BYK-Chemie, the Silwet® brand of silicone surfactants from OSI Specialties and the Zonyl® brand of fluorinated surfactants from DuPont.

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Examples

Example 1

A 5-liter flask was equipped with a mechanical stirrer, thermocouple, N2 inlet, and addition funnels. N-methyl pyrrolidone, 864 gm; isopropanol, 216 gm; and a 15 50% solution of methoxypolyethyleneglycol methacrylate (Bisomer S20W, International Specialty Chemicals) in water, 108 gm, was added to the pot, and were heated to reflux. Feed I [Bisomer S20W, 612 gm], Feed II [methylmethacrylate, 720 gm and styrene, 120 gm], and Feed III [VAZO. 67, 24 gm dissolved in N-methyl pyrrolidone, 216 gm] were started at time 0.0 minutes. 20 Feeds I and II were added over 360 min; Feed III was added over 390 min. After all feeds were complete, the reaction was refluxed and additional 30 minutes. At 420 min. 240 gm of solvent were distilled off, and 272 gm of N-methyl pyrrolidone were added. The final product was a solution of a graft copolymer of methylmethacrylate(60)-co-styrene (10)-g-methoxypolyethyleneglycol 25 methacrylate (30) at 40.6% solids.

Example 2

A 2-liter flask was equipped with a mechanical stirrer, thermocouple, N2 inlet, and addition funnels. A Monomer Solution [isopropanol, 345 gm, a 50% solution 30 of methoxypolyethyleneglycol methacrylate in water (Bisomer S20W, International Specialty Chemicals), 230 gm, methyl methacrylate, 310 gm, and styrene, 25 gm, were placed in an addition funnel. An Initiator Solution [VAZO(52, 10 gm dissolved in N-methyl pyrrolidone, 40 gm] was placed in a second addition funnel. Isopropanol, 190 gm, and 10% of the Monomer 35 Solution and 80% of the Initiator Solution were fed into the pot over 240 min. At 240 minute, the remaining Initiator Solution was fed into the pot over 1 min, and

the reaction was refluxed and additional 60 min. 500 grams of polymer solution were mixed with 293 grams of N-methyl pyrrolidone and heated to remove isopropylalcohol. The final product was a solution of a methylmethacrylate (62)-
5 co-styrene(15)-g-methoxypolyethyleneglycol methacrylate (23) graft copolymer at 37% solids.

Example 3

A 2-liter flask was equipped with a mechanical stirrer, thermocouple, N2 inlet, and addition funnels. N-methyl pyrrolidone, 180 gm and isopropanol, 75 gm were
10 added to the pot and heated to reflux. Feed I [a 50% solution of methoxypolyethyleneglycol methacrylate (Bisomer S20W, International Specialty Chemicals) in water, 180 gm, benzyl methacrylate, 210 gm, N-methyl pyrrolidone, 60 gm and isopropanol, 45 gm], and Feed II [Lupersol® 11, 6 gm dissolved in N-methyl pyrrolidone, 24 gm] were started at time 0.0 minutes. Feed
15 I was added over 360 min; Feed II was added over 390 min. After all feeds were complete, the reaction was refluxed and additional 30 minutes. The final product was a solution of benzyl methacrylate (70) -g-methoxypolyethyleneglycol methacrylate (30) graft copolymer at 38.2% solids.

20 Example 4

A 5-liter flask was equipped with a mechanical stirrer, thermocouple, N2 inlet, and addition funnels. Propylene glycol propyl ether, 1100 gm, and a 50% solution of methoxypolyethyleneglycol methacrylate (Bisomer S20W, International Specialty Chemicals) in water, 75 gm, were added to the pot and heated to reflux.
25 Feed I [Bisomer S20W, 425 gm], Feed II [methyl methacrylate, 750 gm] and Feed III [VAZO(67, 20 gm dissolved in propylene glycol propyl ether, 180 gm] were started at time 0.0 minutes. Feeds I and II were added over 360 min; Feed III was added over 390 min. After all feeds were complete, the reaction was refluxed and additional 30 minutes. The final product was benzyl methacrylate (75) -g-methoxypolyethyleneglycol methacrylate (25) at 38.9% solids.

Example 5

Glossary of Terms:

PnP	Dowanol® PnP (Dow Chemical): propylene glycol n-propyl ether
S-7602	Silwet® L7602 (OSI Specialties): polyalkylene oxide modified dimethyl polysiloxane surfactant
BYK-019	(BYK Chemie): silicone defoamer
BYK-024	(BYK Chemie): silicone defoamer

A cyan ink concentrate was prepared by mixing the first three ingredients together and then processing the mixture on a two roll mill for 30 minutes. The chip was then dissolved in the remaining ingredients listed.

benzyl methacrylate (13)- b -methacrylic acid (10) at 49.7% solids	402.4 g
phthalocyanine pigment	300 g
diethylene glycol	45 g
N-methyl pyrrolidone	426.4 g
Proxel GXL	7.99 g
Deionized water	1861.34 g

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Ink Samples 1 and 2 were then prepared using the concentrate as follows. Amounts are expressed in grams unless otherwise noted.

Component	Ink Sample No.	
	1	2
Cyan Concentrate	20	12
PnP		6
BYK-019	0.9	
BYK-024	0.6	
S-7602	2	
graft co-polymer from example 1		12.1
graft co-polymer from example 2	6.8	
graft co-polymer from example 3	13.1	
N-methyl pyrrolidone	8.3	
hexylene glycol	10	3
diethylene glycol	7	6
Water	38.3	20.9

10 Ink Samples 1 and 2 were then printed using a Trident PixelJet 64 pen onto different textile substrates as identified in the table below and sent for wash testing according to AATCC-61, 1A. Results are reported below.

Ink Sample	Textile	Optical Density (as printed)	Optical Density (after wash)
1	Cotton knit	0.3	0.25
2	Cotton knit	0.55	0.52
2	poly 730	0.51	0.47
2	400M	0.71	0.61
2	poly batiste	0.51	0.41
2	poly/cotton 50/50	0.61	0.56

What is claimed is:

1. A non-ionic graft copolymer comprising a hydrophobic backbone and non-
5 ionic, hydrophilic side chains, said side chains having a number average
molecular weight of at least 500; wherein said graft copolymer is
substantially insoluble in water, but is soluble in an aqueous vehicle
comprising no more than 80% by weight water and at least one organic co-
solvent.

10 2. The graft copolymer of claim 1, wherein the backbone is comprised of
monomers selected from the group consisting of methyl acrylate, methyl
methacrylate, styrene, alpha-methyl styrene, phenyl acrylate, phenyl
methacrylate, benzyl acrylate, benzyl methacrylate, 2-phenylethyl acrylate,
2-phenylethyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl
15 methacrylate, 1-naphthalyl acrylate, 2-naphthalyl acrylate, 2-naphthalyl
methacrylate, p-nitrophenyl acrylate, p-nitrophenyl methacrylate,
phthalimidomethyl acrylate, phthalimidomethyl methacrylate, N-phenyl
acrylamide, N-phenyl methacrylamide, N-benzyl acrylamide, N-(2-
phenylethyl)acrylamide, N-(2-phthalimidoethoxymethyl) acrylamide,
20 vinyl benzoate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, ethyl
methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl
methacrylate, cyclohexyl methacrylate, vinyl acetate, and vinyl butyrate.

25 3. The graft copolymer of claim 1, wherein the side chains have a number
average molecular weight of 1000-2000 and comprise macromonomers
which are
a) soluble in water but are insoluble in non-polar organic solvents;
and
b) made from non-ionic monomers selected from the group consisting
30 of ethoxytriethylene glycol methacrylate, methoxypolyethylene
oxide methacrylate, methoxypolyethylene oxide acrylate,
polyethylenoxide methacrylate, polyethylenoxide acrylate, and N-
vinyl pyrrolidone.

4. The graft copolymer of claim 1, wherein the side chains comprise 15 -
60% by weight of the graft copolymer.

35 5. The graft copolymer of claim 4, wherein the side chains comprise 20 -
50% by weight of the graft copolymer.

6. An aqueous coating composition comprising

5 a) an aqueous vehicle comprising water and at least one organic co-solvent, wherein water comprises no more than 80% by weight of the total weight of the vehicle; and

5 b) a non-ionic graft copolymer comprising a hydrophobic backbone and non-ionic, hydrophilic side chains, said side chains having a number average molecular weight of at least 500, wherein the graft copolymer is soluble in the vehicle but substantially insoluble in water.

10 7. The composition of claim 6, wherein said aqueous vehicle comprises 60-70% by weight of water based on the total weight of the vehicle.

15 8. The composition of claim 6, comprising:

15 a) an aqueous vehicle comprising water, a water miscible pyrrolidone, and a glycol ether, wherein water comprises no more than 80% by weight, based on the total weight of the vehicle;

15 b) a graft copolymer binder having a hydrophobic backbone and non-ionic, hydrophilic side chains, which binder is soluble in the aqueous vehicle but substantially insoluble in water; and

20 c) a surfactant selected from the group consisting of silicon surfactants and fluorinated surfactants.

25 9. The composition of claim 6, wherein the graft copolymer backbone is comprised of monomers selected from the group consisting of methyl acrylate, methyl methacrylate, styrene, alpha-methyl styrene, phenyl acrylate, phenyl methacrylate, benzyl acrylate, benzyl methacrylate, 2-phenylethyl acrylate, 2-phenylethyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, 2-naphthyl methacrylate, p-nitrophenyl acrylate, p-nitrophenyl

30 methacrylate, phthalimidomethyl acrylate, phthalimidomethyl methacrylate, N-phenyl acrylamide, N-phenyl methacrylamide, N-benzyl acrylamide, N-(2-phenylethyl)acrylamide, N-(2-phthalimidooethoxymethyl) acrylamide, vinyl benzoate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, ethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, vinyl acetate, and vinyl butyrate.

10. The composition of claim 6, wherein the side chains have a number average molecular weight of 1000-2000 and comprise macromonomers which are

5 a) soluble in water but are insoluble in non-polar organic solvents; and

10 b) made from non-ionic monomers selected from the group consisting of ethoxytriethylene glycol methacrylate, methoxypolyethylene oxide methacryate, methoxypolyethylene oxide acryate, polyethylenoxide methacrylate, polyethylenoxide acrylate, and N-vinyl pyrrolidone.

11. The composition of claim 6, wherein the side chains comprise 15 - 60% by weight of the graft copolymer.

12. An washfast ink composition for use in printing of textiles, comprising:

15 a) an aqueous vehicle comprising water and at least one co-solvent, wherein water comprises no more than 80% by weight of the total weight of the vehicle;

20 b) a colorant; and

 c) a non-ionic graft copolymer comprising a hydrophobic backbone and non-ionic, hydrophilic side chains, said side chains having a number average molecular weight of at least 500, wherein the graft copolymer is soluble in the vehicle but substantially insoluble in water.

WATER INSOLUBLE NON-IONIC GRAFT COPOLYMERS**Abstract of the Disclosure**

5 A non-ionic graft copolymer has a hydrophobic backbone and non-ionic, hydrophilic side chains having a molecular weight of at least 500, preferably 100-2000 is substantially insoluble in water, but soluble in an aqueous vehicle, and is particularly suited for use in aqueous coating compositions in which water comprises no more than 80% by weight of the vehicle for the composition.

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Water Insoluble Non-Ionic Graft Copolymers

the specification of which is attached hereto unless the following box is checked:

was filed on _____ as U.S. Application No. _____ or PCT International Application No. _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.			
U.S. Provisional Application No.			U.S. Filing Date
I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.			
Application No.			Filing Date
Status (patented, pending or abandoned)			

POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Name: JOSEPH A. TESSARI WILLIAM H. HAMBY	Registration No.: 32,177 31,521
Send correspondence and direct telephone calls to: JOSEPH A. TESSARI	E. I. du Pont de Nemours and Company Legal - Patents Wilmington, DE 19898, U.S.A.

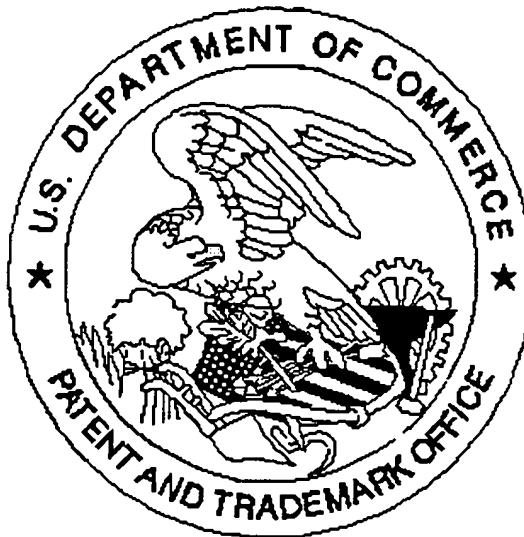
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

INVENTOR(S)

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